Invited Paper

A review of the electrical properties of $Al_xGa_{1-x}N$ materials for UV photodetector applications

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ABSTRACT

In this paper, recent developments in the electrical characterization and doping of $Al_xGa_{1-x}N$ will be reviewed. The properties important for the development of solar-blind UV photodetectors will be stressed. For many of the military and commercial applications of UV photodetectors, the photodetectors must be solar-blind with cutoff wavelengths of less than about 280 nm. This means that for devices based on the $Al_xGa_{1-x}N$ system, the aluminum mole fraction for the active region is nearly 40%. One of the implications for devices is that as the energy gap is increased, doping becomes much more difficult. Therefore, one of the main thrusts of this paper will be the p-type and n-type doping of $Al_xGa_{1-x}N$. In addition to the study of the doping of bulk-like $Al_xGa_{1-x}N$, the use of $Al_xGa_{1-x}N$ based superlattices to reduce the dopant ionization energy will be presented. Because GaN is likely to be used for contact layers in solar-blind devices and as an active layer in visible-blind devices, the electrical properties of this better studied binary material will be reported. The role of electrically active defects and unintentional dopants will also be discussed.

Keywords: GaN, gallium nitride, AlGaN, aluminum gallium nitride, Hall effect, ultraviolet photodetectors, short-period superlattice, p-type doping, magnesium doping

1. INTRODUCTION

$Al_xGa_{1-x}N$ is currently the most promising semiconductor system for truly solar blind photodetectors[1] due to its very wide tunable bandgap. The AlGaN material system has an energy gap ranging from 3.4 to 6.2 eV while the lattice constant only varies by 2.5%. Ultraviolet photodetectors have many military[2] and commercial applications. However, for many of these applications, the photodetectors must be solar blind. This means that the photodetectors must have a cutoff wavelength of less than about 280 nm. Semiconductor based devices would then need energy gaps of over 4.4 eV. In the $Al_xGa_{1-x}N$ system, the aluminum mole fraction, x, required is nearly 40%. For a window layer in a detector transparent down to 240 nm, x>60% is needed. As the energy gap is increased, doping becomes much more difficult, especially p-type doping.

One of the most important devices is the p-i-n photodetector, which requires the ability to dope both p-type and n-type in addition to being able to grow "intrinsic" material. Poor doping can have deleterious effects on device performance. For example, a high contact or material resistance can increase the RC time constant and thereby reduce the maximum operating frequency. In an extreme case, the region near the contacts could be completely insulating, blocking any signal. The relatively high resistivity of a p-$Al_{0.13}Ga_{0.87}N$ recessed window layer in a GaN-based photodiode resulted in electric field crowding and a spatially nonuniform temporal behavior.[3]

Recently, a review paper was published including sections on impurities (hydrogen, carbon, and oxygen) and implants in III-Nitrides.[4] Therefore, these topics will be given limited coverage in this paper. Also, a collection of papers[5-10] emphasizing the theory of doping and the formation of native defects in AlGaN has been published by Van de Walle et al. Some of their key conclusions will be summarized here.

Doping of AlGaN, especially p-type, will be emphasized over GaN doping because of its relative difficulty and utility for solar-blind UV photodetectors. However, GaN has been more extensively studied and may serve as a benchmark and offer insights into some of the issues that must also be addressed in AlGaN. Recent novel doping techniques, such as the use of superlattices, will also be reviewed.

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2. N-TYPE III-NITRIDES

1. GaN:Si

Silicon is the most commonly used intentional n-type dopant in GaN and is incorporated substitutionally on the gallium sites. Silicon is a shallow donor in GaN with reported ionization energies of about 17 meV[11] for a concentration of $3x10^{17}$ cm^{-3}.

Dilute silane (SiH_4) is the most commonly used dopant source for MOCVD.[12] Smooth GaN was grown with carrier concentrations up to 2×10^{19} cm^{-3}. Other sources such as disilane[13] (Si_2H_6) have also been used. In this case, the GaN was doped up to 4×10^{19} cm^{-3}, although surface roughening was observed above 10^{19} cm^{-3}. The incorporation of Si is linear with the flow rate of both of these sources under the conditions reported. It is also possible to dope GaN using silicon by MBE up to very high carrier concentrations of 4×10^{20} cm^{-3} with a corresponding mobility of 20 cm^2/Vs.[14]

2. GaN:Ge

Germanium is also a shallow donor, substituting on the gallium sites. Ionization energies have been reported to be about 19 meV[11] for a concentration of $3x10^{17}$ cm^{-3}. Temperature dependent PL measurements gave a deeper estimate of 34-50 meV for the activation energy.[15]

Dilute germane (GeH_4) is generally used for doping in MOCVD grown films.[12] Doping was less efficient by about an order of magnitude compared to SiH_4 and the surface became rough above 10^{19} cm^{-3}.

3. GaN:O

Oxygen substitutes for nitrogen in GaN. Oxygen has been shown to act as a rather shallow donor in GaN.[16] The oxygen donor in GaN is reported to have an ionization energy of about 29 meV[11], which compares reasonably well with an unintentionally doped HVPE layers of 35 meV determined by optical techniques and very well with another report of oxygen implanted GaN which also gives the ionization energy as 29 meV.[17]

Although several researchers have purposefully added it, most oxygen doping has been unintentional. Oxygen is present to some extent in all growth techniques. In MOCVD, oxygen can be introduced as an impurity in the source materials such as the common water impurity in NH_3, oxygen-containing impurities in the organometallics, or from quartz (SiO_2) at elevated temperatures in a reactive hydrogen environment. Oxygen is also likely to leave substrates such as ZnO and $LiGaO_2$, and has even been suggested to diffuse out of the much more chemically stable and frequently used sapphire (Al_2O_3) substrate. For instance, GaN grown by MOCVD on a $LiGaO_2$ substrate was heavily n-type without intentional doping.[18] It has also been shown that oxygen can diffuse into GaN from a SiO_2 cap, especially along dislocations.[19]

4. GaN:S and GaN:Se

Little research has been done on using the group VI elements other than oxygen as donors in III-Nitrides. Since the non-oxygen group VI elements' electronegativities are low compared to that nitrogen, they would be expected to easily donate their electrons. However, getting these elements to incorporate on the nitrogen site is expected to be difficult because of their relatively large size and different electronegativity. It is conceivable that if they are incorporated at all, it may be on the Ga site as a triple donor. It would then be expected that the donor ionization energy would be higher because of the multivalent nature and the high electronegativity relative to the Ga host atom.

Implantation studies of S into GaN have been performed.[20,21] An early photoluminescence study of implanted GaN did not find any transitions characteristic of sulfur in addition to the peaks attributable to annealing and implantation damage.[20] SIMS analysis showed redistribution of the sulfur implanted into mixed phase GaN after annealing at only 600 C.[21] Assuming that the redistribution and surface loss of sulfur also applies to single phase hexagonal GaN typical of metalorganic chemical vapor deposition (MOCVD) growth, there could be considerable difficulty successfully doping in-situ at the typical growth temperatures of approximately 1000 C. In fact, segregation to the GaN surface was seen in MOCVD in-situ doping using selenium,[22] which has a similar chemistry and atomic size to sulfur. Another selenium doping study of GaN by MOCVD has also been reported.[23] In this study, carrier concentrations up to 6×10^{19} cm^{-3} were obtained.

One report of sulfur doping by MOCVD has also been made.[24] The temperature dependent resistivity of the lightly doped samples is shown in Figure 1. The activation energy was reduced as the H_2S flow was increased. The activation energies were 132 meV for the sample doped with 15 sccm and 50 meV for the sample doped with 30 sccm. The resistivity of the sample doped with 60 sccm was nearly independent of temperature. Heavier doping resulted in surface roughening and higher carrier concentrations.

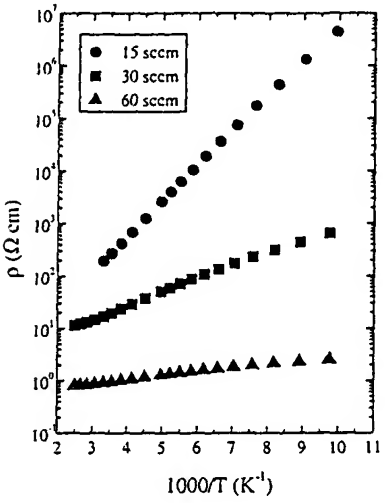

Figure 1. Temperature dependent resistivity of GaN:S samples doped with various amounts of dilute hydrogen sulfide.

5. AlGaN:Si

Again, silicon is a substitutional donor on the gallium and aluminum sites. Theory predicts that silicon does not form a DX center in AlGaN.[5] Silicon is an effective donor in AlGaN for low aluminum concentrations. However, above about 50% aluminum, the material often becomes insulating at room temperature, especially if undoped or lightly doped.

The ionization energy of Si donors in AlGaN was reported to increase from 18 meV for $0<x<0.1$, about 50 meV for x=0.4, to not more than 90 meV for x=0.6.[25] These films were doped to over 3×10^{18} cm^{-3} for x up to 0.5, and about one order of magnitude lower for x=0.6. Unintentionally doped films in contrast were much more resistive with activation energies of 160 meV for x=0.4 and 600 meV for x = 0.6. In another study, MOCVD grown AlGaN:Si with x=0.5 was reported to have a room temperature resistivity of about 2 Ω cm.[26] Films with x=0.2 had a resistivity of about 10^{-2} Ω cm. As seen in Figure 2 an abrupt jump in the activation energy to about 680 meV occurs for x=0.7.[27] It is likely that this x=0.7 film is too lightly doped to be dominated by the silicon donor.

Another MOCVD study of AlGaN:Si saw a maximum resistivity at x=0.48 of 0.9 Ω cm, which then decreased to 0.054 Ω cm for a sample with x=0.58.[28] This AlGaN film had a mobility of 36 cm^2/Vs and concentration of 3.1×10^{18} cm^{-3}. The ionization energy was not reported for these films. Both Si and O were detected by SIMS in quantities sufficient to be significant donors.

It was also reported that for AlGaN:Si grown by MBE, both the carrier concentration and mobility fell by about an order of magnitude as x was increased from 0 to 0.25.[29] The activation energies of the resistivity were reported to be 17, 36, and 54 meV for x=0, 0.08, and 0.18 respectively. These samples had room temperature carrier concentrations in the mid 10^{18} to low 10^{19} cm^{-3} range.

Intentionally doped AlGaN:Si with x=0.44 had a free electron concentration of 10^{19} cm^{-3}, which was nearly temperature independent, indicating a low ionization energy.[30] Another report shows low ionization energies of under about 50 meV for x up to about 0.2.[31]

A recent temperature dependent PL study of undoped AlGaN with x up to 0.22 gave binding energies of about 30 meV for GaN, 120 meV for x=0.22, and an extrapolated value of about 400 meV for AlN.[32] AlGaN was doped to achieve a Si concentration of roughly 5 x 10^{20}cm^{-3} in the films grown by plasma-induced MBE.[33] The activation energy of the resistivity increased in a nearly linear fashion from about 20 meV for GaN to about 325 meV for AlN. Meanwhile the resistivity increased from 10^{-2} Ω cm for GaN to nearly 10^{4} Ω cm for AlN.

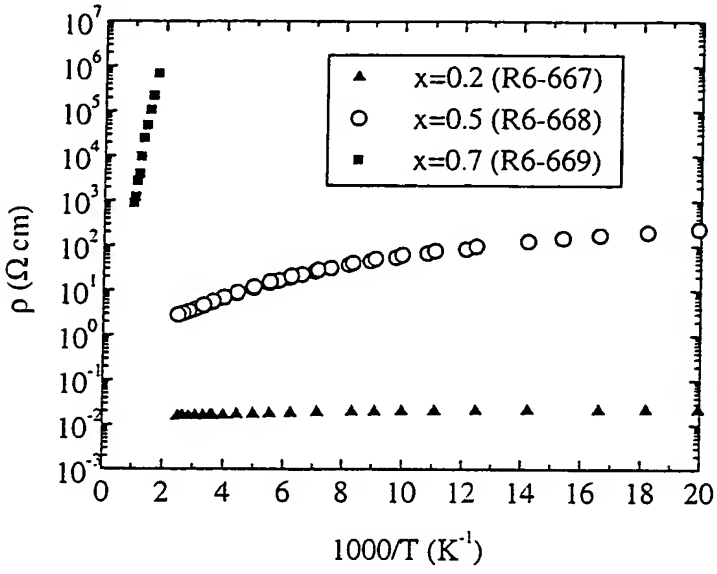

Figure 2. Resistivity as a function of reciprocal temperature for identically silicon doped AlGaN with different aluminum mole fractions.

6. AlGaN:Ge

Germanium is also expected to substitutional for aluminum and gallium. Indeed, germanium has been reported to be a donor in AlGaN.[34] Dilute germane (GeH_4) was used to dope AlGaN with x=0.2 grown by MOCVD up to a room temperature free electron concentration of 3.7 x 10^{19} cm^{-3} and a resistivity of about 4 x 10^{-2} Ω cm. Ionization energies were not reported.

7. AlGaN:O

Oxygen is expected to substitute for nitrogen in the AlGaN lattice. Because of aluminum's strong reaction with oxygen, it is expected to be a very common unintentional dopant in AlGaN. Theory predicts that oxygen becomes a DX center in wurtzite but not zincblende AlGaN.[5] Unintentionally oxygen doped AlGaN was found to have a steadily increasing activation energy as x increased in the range of 0.39 to 0.49.[30] The DX state was predicted to be below the conduction band for x>0.27.

An early report of MBE growth of AlGaN showed the undoped films to be n-type with resistivity increasing from <10^{-3} Ω cm for GaN to nearly 10^{6} Ω cm for x=0.4.[35] The room temperature Hall mobilities were on the order of 10 cm^2/Vs for the maximum x of <0.3. These samples showed little evidence of thermal activation between 77K and 300K. Oxygen may have been the unintentional dopant since water was a very common impurity in ammonia, which was used in this growth. It appears likely that the cause for undoped and lightly doped AlGaN films to be highly resistive is compensation by the deep acceptor level of the oxygen DX center.

3. P-TYPE III-NITRIDES

1. GaN:Mg

Magnesium is a substitutional acceptor on the gallium site. The ionization energy of Mg acceptors has been estimated by fitting temperature dependent Hall effect data to be 208±6 meV for very low doping.[11] This number was obtained by accounting for the Coulomb interaction between the ionized acceptors in heavily doped samples.

It is now widely accepted that hydrogen passivation of magnesium must be removed in order to achieve p-type GaN. This was first achieved by low energy electron beam irradiation.[36] Subsequently, it was also found that annealing in a hydrogen free atmosphere could also be used to eliminate the passivation.[37] MBE growth has been able to show p-type doping without a post-growth anneal. More recently, atmospheric pressure MOCVD using ammonia but no hydrogen during the growth has also demonstrated as-grown p-type GaN.[38] (Films grown under hydrogen and cooled under nitrogen remained resistive.) Thermopower and conductivity measurements showed the Mg-H complexes to increase the activation energy to 0.52 eV.[39]

Diffusion of magnesium in GaN has been shown not to be a problem under normal MOCVD growth conditions.[40] However, evidence of a reactor memory effect was observed as a tail in the magnesium profile.

Recently, a study of GaN doped with a wide range of magnesium concentrations during MOCVD growth was studied by variable temperature Hall effect.[41]

2. GaN:Zn, GaN:Be, and GaN:Ca

Theoretically, alternative acceptors to Mg have been studied for substitution on the Ga site.[9,10] They found Zn and Ca to have higher ionization energies than Mg. Also, Ca would have poor solubility. Be was determined to have similar solubility and ionization energy to Mg, but interstitial donors could form.

Experimentally, doping with acceptors other than Mg has been limited.

Insulating GaN:Zn layers have been grown by HVPE.[42] Ionization energies of 0.18 eV and 0.7eV were obtained by resistivity measurements utilizing a mesa structure. In another experiment, a 0.34 eV ionization energy was determined by PL measurements.[43]

An optically determined ionization energy for Be acceptors in GaN grown by MBE was about 90 meV.[44] Other values, also based on luminescence, were larger at 150 meV[45] and 250 meV[46]. A theoretical calculation puts the Be ionization energy at about 60 meV.[47]

Calcium doping has been performed by ion implantation.[17] An ionization energy of 169 meV was reported.

3. GaN:C

Carbon, substituting on the nitrogen site, would be an acceptor. Few reports have been made of intentional carbon doping of GaN. CCl_4 was used to dope GaN during metalorganic MBE growth.[48] A maximum concentration of $3x10^{17}$ cm^{-3} with a mobility over 100 cm^2/Vs was reported. Another attempt used a graphite filament as the carbon source during MBE growth.[49] These films remained n-type with increased compensation and yellow luminescence. A PL study gave a value of 230 meV for a residual acceptor that was attributed to carbon.[50] Also, MBE growth using methane as the carbon dopant source was used to achieve semi-insulating layers.[51] In another report, it was implied that more carbon might be introduced using TMGa than using TEGa during MOCVD growth of GaN, leading to insulating films or higher compensation.[52]

4. AlGaN:Mg

Both experimentally and theoretically, the Mg acceptor level becomes progressively deeper as x is increased in AlGaN. Theory predicts that the ionization energy increases from 0.2 to 0.4 eV as x is increased from 0 to 1, but formation of an AX center does not occur.[10]

As seen in the data of Figure 3 for a set of MOCVD grown samples the room temperature resistivity increased in a log-linear fashion from about 2 Ω cm to about 10^5 Ω cm as x was increased from 0 to 0.3.[26] Figure 4 shows that there is a rapid increase in the ionization energy as x is increased.

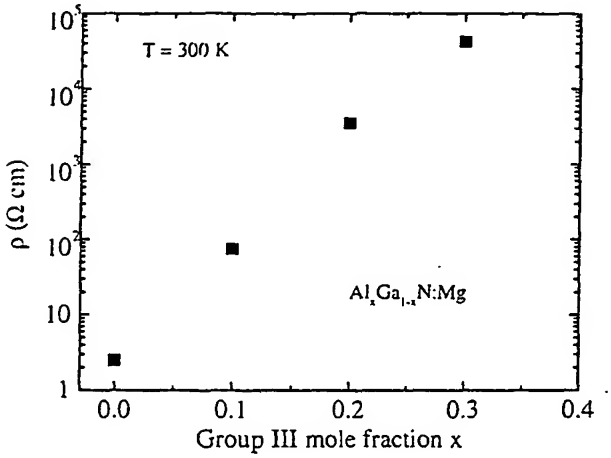

Figure 3. The room temperature resistivity of AlGaN increases by several orders of magnitude as the Al content is increased.

An $Al_{0.08}Ga_{0.92}N$ layer doped with magnesium was reported to have an ionization energy of 192 meV compared to 157 meV for a similarly doped GaN layer.[53]

For $Al_{0.15}Ga_{0.85}N$, the ionization energy was roughly estimated to be 250 meV through room temperature measurements alone.[54] This sample had a resistivity of 15 Ω cm at room temperature with mobility of about 8 cm^2/Vs and concentration of about 6×10^{16} cm^{-3}. Attempts at higher doping did not result in higher hole concentrations even though the Mg concentration increased as measured by SIMS increased.

In MBE grown samples with an atomic magnesium concentration of about 5×10^{19} cm^{-3} the room temperature showed an increasing activation energy of the resistivity with increasing aluminum concentration.[33] The activation energies were 170, 280, and 360 meV for x=0, 0.12, and 0.27 respectively. In another set of MBE grown samples the resistivity increased to over 2000 Ω cm for x=0.2 from a value of about 10 Ω cm for lower aluminum concentrations.[29]

In contrast with results from other groups, a room temperature hole concentration of 10^{17} cm^{-3} has been reported for $Al_{0.33}Ga_{0.67}N$:Mg.[31] They also report ionization energies to be lower than that expected by a linear increase in effective mass with higher x. Their ionization energies remain under about 200 meV for x up to 0.33.

Evidence has been seen for competition between Mg and Al during MOCVD growth.[40] This results in less abrupt profiles and reduced concentrations.

Ion implantation and annealing of $Al_{0.12}Ga_{0.88}N$ with Mg and C resulted in highly resistive layers, with no indication of activation of acceptors.[55]

5. AlGaN:Zn

Zinc related photoluminescence[56] and cathodoluminescence[57] peaks were observed in AlGaN ($x<0.25$ and $x<0.3$ respectively), but the electrical properties were not reported.

6. Co-doping

Co-doping has been proposed to have several potential benefits that would produce additional acceptors in GaN. These include a lower acceptor ionization energy, higher solubility of acceptors, and reduced scattering. Si and O have been studied theoretically as co-dopants for Mg or Be in GaN.[47,58-59]

An incredible report of cubic GaN codoped with Be and O grown on GaAs by MBE was made claiming a resistivity of under 0.02 Ω cm.[60] The order of magnitude improvement was due primarily to an increase in the hole mobility (150 cm^2/Vs), rather than a reduction in ionization energy (170 meV) or increase in hole concentration (10^{18} cm^{-3}).[61] The mobility increase was attributed to scattering from dipoles rather than simple ionized impurities. (The GaAs substrate was etched away for the Hall measurement.) SIMS measurements revealed concentrations of about 5 x 10^{20} cm^{-3} for both Be and O.

Bulk GaN grown at high temperature and pressure has been simultaneously doped with very high concentrations of magnesium and oxygen. The result was insulating material. Evidence was found both for formation of neutral MgO[62] and for ionized magnesium acceptors compensating the oxygen donors.[63]

Using a different type of codoping, a photoluminescence study of As+C, As+Mg, and Mg+C was made.[64] Ionization energies were reported of 180 meV for both using As co-implants and 130 meV for the Mg+C co-implant.

7. Magnesium doped AlGaN superlattices

The first use of superlattices to reduce the dopant ionization energy was reported for short-period superlattices of AlGaN/GaN doped with magnesium.[65] This work used short-period superlattices, with minibands far enough separated from the GaN conduction band to give an increase in the minimum absorption energy above that of GaN. The resulting ionization energies are plotted in Figure 4 as a function of the cutoff wavelengths of the material.

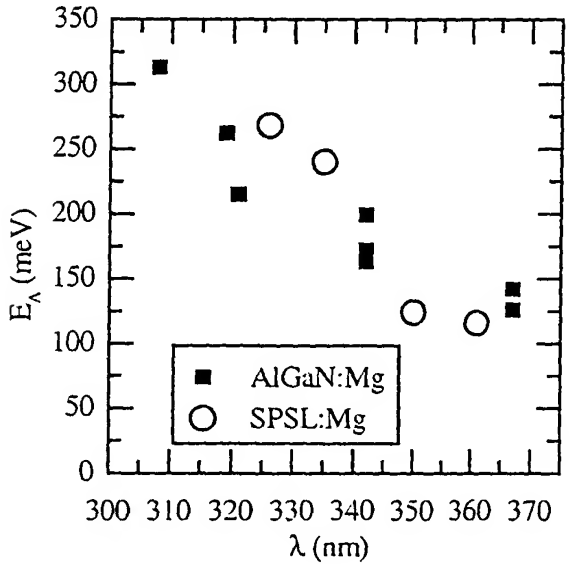

Figure 4. Acceptor ionization energies as a function of optical absorption edge (50% transmission) of bulk-like AlGaN:Mg compared with Mg doped GaN/AlGaN short-period superlattices.

Also, very low acceptor ionization energies have been demonstrated in longer period AlGaN/GaN superlattices doped with magnesium.[66,67] This is seen in Figure 5 by the nearly temperature independent carrier concentration in the superlattice. The longer periods induce large band bending due to piezoelectric effects. For an 8.8 nm/ 8.8 nm AlGaN/GaN superlattice with

x=0.2, the spatially averaged carrier concentration is over 2 x 10^{18} cm^{-3} with a corresponding sheet carrier concentration of about 4 x 10^{12} cm^{-2}. Due to their long periods, these structures are not expected to have effective bandgaps any larger than GaN. Also, tunneling through the barriers and formation of minibands would be negligible.

Another report[68] of enhanced doping using $Al_xGa_{1-x}N$/GaN superlattices due to the piezoelectric effect with long period superlattices resulted in a maximum sheet hole concentration per period of $8x10^{12}$ cm^{-2}. The sheet hole concentrations increased as the superlattice period and the aluminum concentration were increased up to 24 nm / 12 nm and x=0.15. The sheet concentrations remained roughly constant as they were further increased. The equivalent averaged hole concentration was 3 x 10^{18} cm^{-3} while the magnesium concentration was estimated to be 2 x 10^{19} cm^{-3} by SIMS. Only room temperature Hall effect measurements were performed, so no information on the activation energy was obtained.

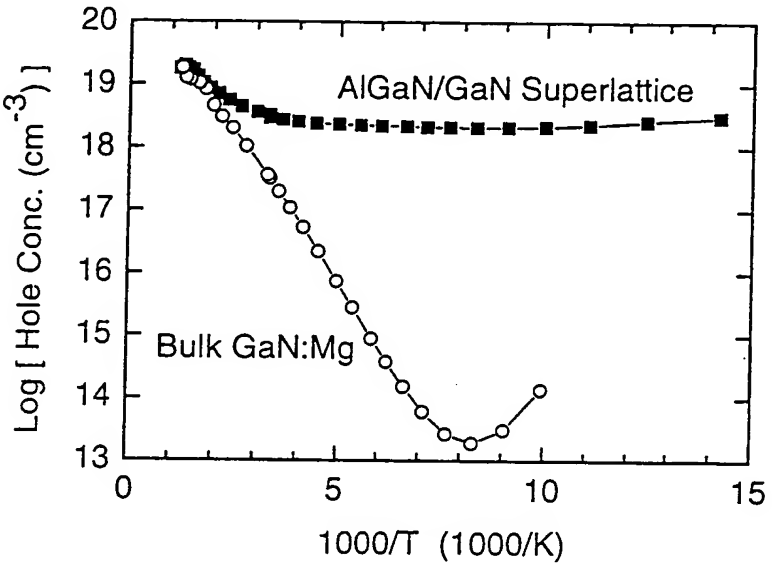

Figure 5. Hole concentration as a function of temperature, as determined by variable temperature Hall effect measurements. The solid squares are values obtained from a uniformly-doped, MOCVD-grown $Al_{0.2}Ga_{0.8}N$/GaN superlattice with L = 88 Å, the open circles represent data from a bulk Mg-doped GaN film grown under similar conditions. From reference 66.

Activation energies were determined for a set of 10 nm / 10 nm superlattices.[69] The resulting ionization energies for x=0.2 and x=0.1 were about 58 meV and 70 meV respectively compared to about 200 meV for bulk GaN obtained by a simple Arrhenius slope which probably overestimated the energies. The samples had an estimated magnesium concentration on the order of 10^{19} cm^{-3}. The average room temperature mobility and average concentration were 1 cm^2/Vs and 3 x 10^{18} cm^{-3} respectively for the x=0.2 sample. This gives a sheet hole concentration per period of about 6 x 10^{12} cm^{-2}.
Carrier concentrations have been simulated for long period superlattices with abrupt and parabolically graded interfaces.[70]

Also, lateral transport could be greatly enhanced if two-dimensional hole gases are created because of enhanced mobility. The mobility was calculated[71] to be over 5000 cm^2/Vs for barriers with up to 15% aluminum concentration and carrier concentrations of over $5x10^{12}$ cm^{-2}. Alloy disorder scattering limits the mobility for high carrier densities in these calculations.

4. DEFECTS AND DEEP LEVELS

1. Vacancies

In near equilibrium growth techniques, it has been shown theoretically that only compensating vacancies will be formed and are not responsible for the background concentrations of unintentionally doped sample.[7] For example, N vacancies will only have significant concentrations in p-type material and therefore are not generally responsible for the n-type background concentration in GaN. (Oxygen and silicon, known shallow donors, have in most cases been detected in sufficient amounts

to account for the carriers.) The gallium vacancy was suggested as the source of the broad yellow photoluminescence observed in many n-type GaN films.[15,72]

Positron annihilation studies have detected gallium vacancies in n-type bulk GaN grown at 1500 C.[63] The unintentionally doped sample had a carrier concentration on the order of $5x10^{19}$ cm^{-3}, in good agreement with the oxygen concentration determined by SIMS. The V_{Ga} concentration measured in this sample was $2x10^{17}$ cm^{-3}. By doping heavily with Mg, the samples became semi-insulating with nearly equal Mg and O concentrations of 10^{20} cm^{-3}. By lowering the Fermi level in this way, the V_{Ga} concentration was reduced to less than 10^{16} cm^{-3} as would be expected by the theory.

The nitrogen vacancy donor ionization energy is 64±10 meV as determined by fitting temperature dependent Hall effect data using a electron irradiated GaN sample.[73]

Plasma exposure has been shown to introduce shallow donor states in p-type GaN.[74]

2. Threading dislocations

Threading dislocations have been associated with deep acceptor levels. For instance, a reduction in dislocations through the use of interlayers resulted in increased mobility and reduced yellow emission.[75] The effect of scattering by charged acceptors in n-type GaN is to reduce the electron mobility.[76]

3. Rare earth doping

Researchers have doped GaN with several different rare earth elements including Er, Eu, Dy, Pr, and Tm[77] in order to produce luminescence in the visible and infrared portions of the spectrum. A recent issue of the MRS Bulletin was devoted to this topic.[78] These dopants are generally not considered for n-type or p-type doping, so they will not be discussed further here.

5. CONCLUSIONS

Fundamental doping issues continue to limit device performance. One of the major limitations to achieving high carrier concentrations is the large thermal ionization energies of dopants, especially in p-type material and in high aluminum mole fraction material. Novel solutions for this problem including superlattices and co-doping are currently being studied. Recent results indicate that adequate n-type doping should be achievable for the aluminum concentrations required for most UV photodetectors through conventional Si doping techniques.

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